



# Catalytic effect of tin oxide nanoparticles on cellulose pyrolysis



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## ABSTRACT

In this study, SnO<sub>2</sub> nanoparticles were synthesized via hydrothermal method and used as a catalyst for cellulose (model biomass) pyrolysis. Effect of catalyst on the yields of pyrolysis products was discussed in details. Optimum catalyst to biomass ratio was found as %5 (w/w). The pyrolytic oil (tar) was characterized by Gas chromatography–Mass spectrometry (GC–MS) while the gaseous products were characterized with micro Gas Chromatography (μGC) to understand the catalytic ability of SnO<sub>2</sub> nanoparticles. The results indicate that gaseous product yields significantly increase while the char yield decreases. Although the tar yields don't change significantly in the uncatalysed runs, the product distribution in tar decreases in the presence of catalyst.

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## 1. Introduction

Nowadays, biomass energy is the most promising alternative to fossil fuels and it is the third biggest primary energy source after coal and petroleum [1,2]. Theoretically, the amount of CO<sub>2</sub> released during biomass conversion is equal to the amount of CO<sub>2</sub> absorbed by plants during photosynthesis, for this reason biomass energy is a known CO<sub>2</sub> neutral energy type [3].

Biomass conversion techniques can be separated into four basic categories: direct combustion processes, thermochemical processes, biochemical processes and agrochemical processes. One of the most preferred techniques is thermochemical conversion process. These processes can be subdivided into gasification, pyrolysis, supercritical fluid extraction and direct liquefaction [4]. Pyrolysis is the thermal decomposition of substance in oxygen-free environment and it has an extremely important place among thermochemical conversion technologies. Pyrolysis studies are gaining increasing importance, as it is not only an independent process, but it is also a first step in the gasification or combustion process [5]. The pyrolytic oil (tar) contains many valuable hydrocarbons, therefore it can be used as a source of chemical feedstock. Moreover, due to its high calorific value of [6,7], tar can also be used as a fuel after refining. From the perspective of energy, one of the most valuable products obtained is gaseous products, the composition of which includes H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>4</sub>H<sub>10</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>2</sub>H<sub>2</sub> etc. Espe-

cially hydrogen is green and efficient energy source but due to high production costs and storage problems, its use is limited. One of the critical point about future is decreasing of the production costs of gases, such as hydrogen and methane, and obtaining with high calorific value products from renewable sources.

Features of pyrolytic products can be upgraded via catalytic pyrolysis [8–11]. For upgrading the pyrolytic products, different kinds of catalysts were used such as clays [12,13] (ZSM-5, MCM-41), supported metals [14,15] (Pt, Ni, Pd etc.) and salts [16] (Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, ZnCl etc.).

In recent years, nano size metal oxides have attracted extensive attention in various catalytic processes due to their unique properties such as high specific surface area, strong base strength, quantum size effect, nanocrystal shape and polar surface [17–19] but they are not widely used in catalytic pyrolysis of biomass [20]. So catalytic behavior of nano metal oxides on cellulose pyrolysis should be identified. In our previous study, nano SnO<sub>2</sub> was used as catalyst for pyrolysis of hazelnut shell and confirmed to have some good catalytic activity. Obtained results show that nano SnO<sub>2</sub> catalyst promoted char reduction and gaseous product formation when compared with bulk form. This behavior of nano SnO<sub>2</sub> can be explained by accelerated primary and secondary decomposition reactions of hazelnut shell due to the nano size and large external surface area of the nanoparticles [21]. Nowadays, it has been seen an increase in papers about metal oxide catalyzed pyrolysis [17,20–32] in the literature and also some of them about bulk metal oxides [17,23,25–28,32]. The aim of this study is, using SnO<sub>2</sub> nanoparticles as a catalyst in the conversion of cellulose which is the major component of biomass (40–60% (w/w)) [33] and

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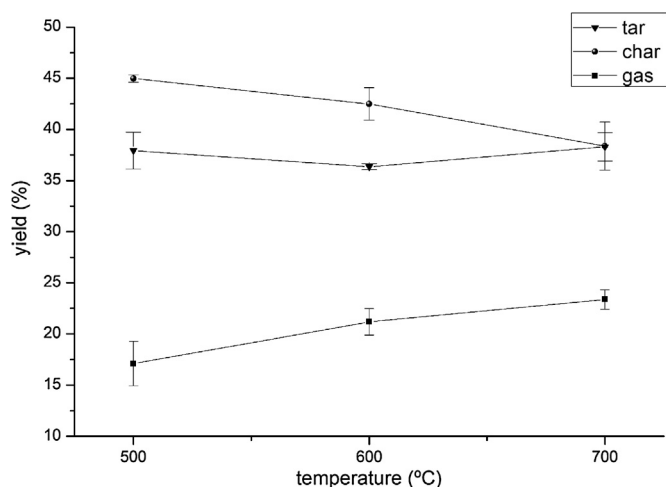


Fig. 1. Cellulose pyrolysis products yields without catalyst in three different temperatures (%).

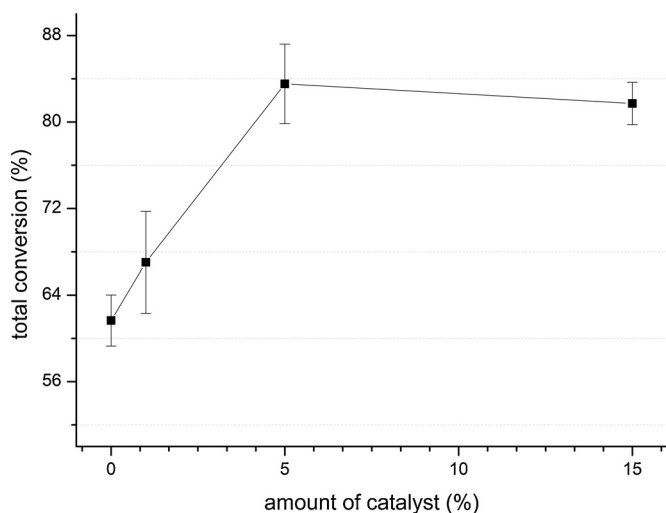


Fig. 2. Effect of different amount of catalyst on total conversion ratio at 700 °C.

determining the effects of products distribution, with this respect, nano SnO<sub>2</sub> was used as a catalyst for the pyrolysis of cellulose to test whether they had the capability to upgrade the properties of pyrolytic oil and gaseous fractions. Characterization of the tar and gaseous fractions was performed using GC/MS and micro-GC. The catalytic and non-catalytic products were compared to reveal the catalytic capabilities of these catalysts.

## 2. Experimental

### 2.1. Materials

Sn powder (J.T. Baker), H<sub>2</sub>SO<sub>4</sub> (Sigma Aldrich 98%) and H<sub>2</sub>O<sub>2</sub> (Merck 35%) were used for synthesis of SnO<sub>2</sub> nanoparticles. Micro-crystalline cellulose powder (Sigma Aldrich) was used for pyrolysis experiments as a model biomass. All chemicals were analytical grade and used without further purification.

### 2.2. Catalyst preparation and characterization

Hydrothermal synthesis of SnO<sub>2</sub> nanoparticles as well as transmission electron micrographs (TEM) and X-ray diffraction patterns (XRD) were described in our previous study [21,34]. The surface

areas of the particles were determined by a Sorptometer (Nova 2200, Quantachrome).

### 2.3. Experimental set-up of pyrolysis system

Pyrolysis experiments were performed by the system given in our previous study [21]. The pyrolysis reactor is made of stainless steel and it has a 2 mm wall thickness, 240 mm length and 20 mm diameter. 3 g of cellulose was directly mixed with the specified amounts of catalyst (1, 5, 15% (w/w)). The mixture was loaded into the reactor. Before the heating, whole pyrolysis system was purged by nitrogen about 30 min with a flow rate of 30 mL/min. The tubular furnace was heated from room temperature to intended temperature with the heating rate of 50 °C/min. Pyrolysis procedure was continued for 1 h. At the end of 1 h no further liquid or gaseous product was observed. The effluent stream from the reactor was connected to condenser system and condenser system was put into ethanol/ice bath (−8 °C). The tar was collected in the condenser and recovered by washing with 50 mL dichloromethane and then extracted with 50 mL water. Dichloromethane phase was used for analysis. Gaseous product was accumulated in tedlar bag connected to the output of the system. All experiments were repeated twice. The amount of residual solid product was defined as the char while the mass of liquid product collected in the condenser was defined as the tar. The amounts of char and tar were divided by the mass of the initial mass of cellulose in order to obtain char and tar yields respectively. The yield of gas was calculated by difference.

### 2.4. Analysis of gaseous products

The composition of the gaseous product was analyzed with SRA Instruments T-3000 model micro GC. μGC consists of two modules with TCD detector. The first module (MS5A) was set at 90 °C and use for determination of He, H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, CO and CH<sub>4</sub> and use Argon as the carrier gas. The second module (PPU) was set at 70 °C for the separation of CO<sub>2</sub>, H<sub>2</sub>O (g) and C1–C4 hydrocarbon gases with using Helium as the carrier gas. Analysis results obtained from instrument (% mole) were converted to [mg gas/g biomass] as specified in Eqs. (1)–(3).

$$\text{Total gas amount (g)} = [\text{initial mass of cellulose (g)} \times \text{gas yield (\%)}] \div 100 \quad (1)$$

$$A = \frac{\text{total gas amount (g)}}{\langle M \rangle \text{ of gaseous products (g.mol}^{-1})} \quad (2)$$

$$\frac{\text{mg gas}}{\text{g cellulose}} = \left( \frac{A \times \text{mole\% result of the gas}}{100} \right) \times \frac{\text{molar mass of the gas}}{\text{initial mass of cellulose}} \quad (3)$$

### 2.5. Analysis of liquid products

GC–MS analysis of the liquid products (dichloromethane phase) was performed by Shimadzu GC–MS–QP2010 Plus with a HP-5MS (30 m × 0.25 mm × 0.25 μm) capillary column. Helium was used as the carrier gas. The amount injected was 1 μL and split ratio was 4:1. The oven temperature was set to 50 °C for 5 min, then raised to 300 °C with 5 °C/min and stayed at 300 °C for 15 min. Total run time was 70 min and flow rate was 0.8 mL/min. Mass spectra were recorded under 70 eV electron ionization and 50–750 m/z interval. The mass spectra obtained by GC–MS was interpreted based on an automatic library search (Wiley & NIST) and discussed with related literature data.

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